(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 22 February 2001 (22.02.2001)

PCT

(10) International Publication Number WO 01/13389 A1

(51) International Patent Classification7: B01D 15/08

H01G 9/00.

- (74) Agent: CROWLEY, Richard, P.; 901 Main Street, P.O. Box 901, Osterville, MA 02655-0901 (US).
- (21) International Application Number: PCT/US00/20768
- (22) International Filing Date:

29 July 2000 (29.07.2000)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 60/148,885

13 August 1999 (13.08.1999) US

- (71) Applicant and
- (72) Inventor: ANDELMAN, Marc, D. [US/US]; One Parkton Avenue, Worcester, MA 01605 (US).

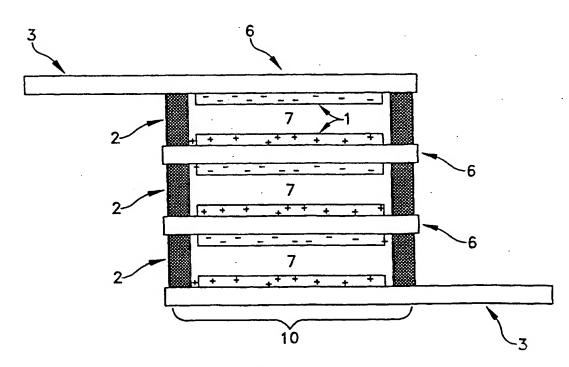
- (81) Designated States (national): AU, CN, JP, MX, US.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:

With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FLOW-THROUGH CAPACITOR, SYSTEM AND METHOD



(57) Abstract: A flow-through capacitor and fluid for the purification system wherein the flow-through capacitor comprises a plurality of individuals, electrolyte-isolated cells (7), and the cells are electrically connected in series in a cartridge holder.

Description

FLOW-THROUGH CAPACITOR, SYSTEM AND METHOD Reference to Prior Application

This application is a based on and claims priority from U.S. Provisional Patent Application Serial No. 60/148,885, filed on August 13, 1999, and is hereby incorporated by reference.

Background of the Invention

Flow-through capacitors are represented in Andelman U.S. Patent Nos. 5,192,432, issued March 9, 1993; 5,196,115, issued 10 March 23, 1993; 5,200,068, issued April 6, 1993; 5,360,540, issued November 1, 1994; 5,415,768, issued May 16, 1995; 5,547,581, issued August 20, 1996; 5,620,597, issued April 15, 1997; 5,779,891, issued July 14, 1998; Otowa U.S. Patent 15 No. 5,538,611, issued July 23, 1996; Farmer U.S. Patent No. 5,425,858, issued June 20, 1995; and Benak U.S. Patent No. 3,658,674, issued April 25, 1972. These patents all describe flow-through capacitors that electrically comprise a single electric cell per cartridge holder. Scale up to larger 20 size causes these capacitors to draw high amperage power. High amperage power requires extra thick wires and buss bars and expensive power supplies. Therefore, a need exists for a flow-through capacitor which can utilize less expensive, more economical, higher voltage, lower amperage power for a given watt rating. 25

The aforementioned prior art patents describe single cell capacitors with one cell per cartridge holder, utilizing multiple, parallel-connected anode and cathode layers per cell. A cell comprises at least one anode and cathode layer with an ionically conducting electrolyte that operates within the rated cell voltage. This rated voltage is usually set below the level where electrode deterioration takes place or other undesirable electrochemical reactions occur. Where multiple electrode layers exist, these layers are usually connected in parallel. In the flow-through capacitor, this electrolyte is the working fluid that is being treated. In

order not to exceed the rated voltage per cell, this fluid must be electrically isolated from the fluid in any other cell. In order to electrically connect prior art capacitors in series, individual flow-through capacitor cartridge holders must be chained together. Fluid flow and electricity must be distributed equally between cells, so that the individual cell voltages do not become unbalanced. This often requires that each cell be individually monitored and controlled. For example, Fig. 15 of Andelman U.S. Patent No. 5,799,891 pictures a flow-through capacitor system with three flowthrough capacitors in individual cartridge holders. cartridge holder contains one cell, typically made from multiple, parallel-connected electrodes. Use of an additional cartridge holder per cell increases the cost of seriesconnected, flow-through capacitors that comprise multiple cells, yet are self-contained in one cartridge holder. Also, a need exists for a series-connected, flow-through capacitor that can operate at voltages higher than that of a single cell, yet within a single cartridge holder, where the individual cells are electrically isolated from one another.

10

15

20

25

35

Otowa U.S. Patent No. 5,538,611 and Farmer U.S. Patent No. 5,425,858 both utilize gaskets to isolate the fluid flow path. Otowa utilizes single electrode layers sealed by a gasket. However, Otowa does not use double-sided electrodes to provide a capacitor of enhanced voltage internal to a single cartridge holder. Farmer utilizes gaskets and many double-sided, internal electrode layers, but these layers are connected in parallel.

Summary of the Invention

The invention relates to a flow-through capacitor, system and method.

It is desirable to provide a series-connected, flow-through capacitor to allow the use of more energy and cost efficient electrical power within a single, easy to manufacture cartridge.

The invention is also related to a series-connected, flow-through capacitor with multiple individual electrolyte-isolated cells and which capacitor is self-contained in a single cartridge holder.

An additional advantage of the present invention is that only the electrical leads at the either end of the electrode stack need be connected to a power supply, yet voltage may be higher than the single cell rating.

5

10

15

20

25

The invention comprises a flow-through capacitor for the purification of an electrolyte fluid, which capacitor includes: a cartridge holder; an inlet in the holder for a fluid to be purified; an outlet in the holder for the withdrawal of a purified fluid; a discharge outlet; and a plurality of electrolyte-isolated individual cells, each cell composed of an anode-cathode pair of electrode material in a stacked arrangement within the holder, and the individual cells are electrically connected in series.

In the present invention, the electrodes of the capacitor are series-connected, due to sealing gasket, so that the intermediate electrodes of the capacitor simultaneously comprise an anode on one side and a cathode on an other side.

The invention will be described for the purpose of illustration only in connection with certain illustrated embodiments; however, it is recognized that various changes, modifications, additions, and improvements may be made in the illustrative embodiments without departing from the spirit or scope of the invention.

Description of the Drawings

- Fig. 1 is an exploded perspective view of the electrode 30 layers and gaskets of the invention to form series-connected cells;
 - Fig. 2 shows top plan and side views of individual electrodes and current collectors;
- Fig. 3 schematically illustrates a charged capacitor of the invention with individual cells;

PCT/US00/20768 WO 01/13389

Fig. 4 is a schematic, perspective sectional view of a flow-through capacitor stack of the invention;

Fig. 5 is a schematic illustration of a flow-through capacitor system of the invention; and

Fig. 6 is an illustrative perspective sectional view of a flow-through capacitor of the invention with an illustrated plan view of an electrode, spacer, or current collector shape.

5

25

Description of the Embodiments

Fig. 1 shows the arrangement of layers and gaskets used to isolate the electrodes, in order to utilize both sides of 10 the electrodes 1, yet form cells with single facing anode and cathode layers per cell. The end electrodes are single-sided and may be exposed to the air to form the top fluid seal of the cartridge holder. This method of construction allows the electrical isolation of individual cells by using the 15 electrode or optional current collector in combination with gaskets 2 to form a fluid-tight compartment, whereby the electrolyte from each cell is electrically isolated from the neighboring cells. End electrodes may be drawn out into a Gaskets 2 may have an optional nonelectrical 20 lead 3. conductive, but ionically- conductive spacer layer 4. Gaskets may have flow holes 5.

Fig. 2 shows the individual electrodes 1 and the optional current collectors 6.

Fig. 3 shows individual cells 7 formed electrostatically when the capacitor is charged. Gaskets 2 seal against the optional current collector 6 or directly to the conductive material used for electrodes 1. The end electrodes 1 are single-sided, and the internal electrodes 1 are double-sided. However, from the electrical point of view of each, all the 30 electrodes 1 are single-sided, providing only one anode and one cathode layer per each individual electrical cell. In the prior art, double-sided electrodes were either an anode or cathode, but not an anode on one side and a cathode on the other side, as in the present invention. Each electrode 1, 35

however, may be represented by multiple parallel electrodes, in order to provide thicker cells with better flow properties, yet while maintaining a capacitor that operates at enhanced voltage within a single capacitor cartridge holder. The cartridge holder is formed by the gaskets or may be an additional holder into which with gasket assembly of Fig. 3 fits. Once a flow-through capacitor stack 8 is built that has the proper voltage and flow characteristics, this may be used as modules, and in turn, be further connected together, both electrically and in a fluid flow sense, either in series or parallel, or in any combination thereof. For example, several stacks may be connected electrically in parallel, yet the fluid flow may be in series.

10

15

20

25

35

Conductive material may be a high surface area conductor greater than 1000 grams per square meter B.E.T. or a high specific capacitance, yet low surface area material, e.g., 10 to 1000 grams per square meter B.E.T. or may be any conductive material, such as titanium, tantalum, and graphite coated with ruthenium oxide or ruthenium oxide, fluorocarbon fiber sheet material, without regard to surface area when used, for example, to remove contaminants via electroplating instead of electrostatic absorption.

Enhanced voltage through connection in series also aids in energy recovery by allowing the use of more energy efficient, higher voltage DC to DC converts. To do this, two One charges with capacitors are operated in tandem. electricity and purifies the solution and the other discharges while it desorbs a concentrated waste. When a flow-through capacitor is ready to be regenerated, it is electrically discharged. This energy can be recovered and used to charge another capacitor during its charge/purification cycle. order to do this, the voltage of the discharging cell must be increased, so that it may be sufficiently high to charge the DC to DC This may be done with purifying capacitor. converters. These may use, for example, inductor coils or

transformers, in order to increase and regulate the voltage. Use of DC to DC converters may also be used in any flow-through capacitor, either parallel, individual cells connected in series or the series design of the present invention.

5

10

15

20

25

30

35

Fig. 4 shows an assembled capacitor stack 8, cut lengthwise down the middle, comprised of six cells. The flowthrough capacitor of the invention may be comprised of any number of cells, but from a practical standpoint, is usually less than two hundred cells. Each individual cell has to be similar in size in order to balance the voltage. Flow rates and amounts of material purified should match between each cell as much as possible and in order to keep the voltage Flow, shown by an arrow, is balanced between the cells. through inlet 9, into fluid flow baffle 10, through individual gasket holes 5 and out baffle 10 and exit 11 (hole not shown). Gaskets 2 seal each individual cell 7, so that an electrically conductive path does not form between cells 7 through the electrolyte represented by the working solution. The purpose of baffle 10 is to distribute flow between each cell, yet provides a long conductive path length through the electrolyte This long path through the electrolyte between the cells. between cells 7, holes 5, and electrical path in baffles 10 has a high resistance and serves to electrically isolate the individual cells 7. Baffle 10 may contain a serpentine flow path or other means, in order to lengthen the flow path between cells, so that the resistance is low enough to prevent significant current flow between cells. Generally, this flow path should be long enough and thin enough, so that the electrical resistance is more than 1 ohm and preferably, more than 100 ohms.

Fig. 5 is a flow-though capacitor system of the invention with power supply 27 connected via wires 12 to capacitor stack 8 via screw 13, nut and bolt assembly 14, and extending leads 3. Alternatively, wires may be welded, if appropriate, for the particular material involved. Pump 15 controlled by

Example 1

Wastewater from a semiconductor plant is neutralized and fed into a 10 cell capacitor stack of the invention at a rate of 1 gallon per minute. The capacitor is made from ruthenium-coated, tantalum-conductive, ceramic electrodes connected to a 10 volt power supply. These electrodes are integral to the current collector, so they do not need an additional current collector. The capacitor is initially charged at 4 volts for the first minute, then at 10 volts after 1 minute. Corn syrup purified from ash is collected in a collection tank. During regeneration, the electrodes are short-circuited in order to desorb the concentrated waste into the water, which is disposed of down the drain.

Example 2

10

A 20 cell, flow-through capacitor made from 20 cells of activated carbon cloth and graphite foil current collector is used to purify whey at 1 gallon per minute, connected to a 40 volt power supply. Desalted whey is collected in a container. During regeneration, the whey is replaced with water, and the electrodes are short-circuited in order to desorb the concentrated waste into the water, which is disposed of down the drain.

Example 3

A 5 cell, flow-through capacitor made from aligned 25 nanotubes is used to purify sulfate from well water at 2 volts. The voltage per cell is 0.4 volts.

Example 4

A 100 cell, electrode stack made from copper foil is used to purify plating waste containing 20 ppm nickel metal. The stack is run at 20 volts or 0.2 volts per cell. Nickel metal plates onto the stack allow purified water to pass through. The electrodes in this capacitor are fairly stiff and do not

logic means 16 pumps the working fluid to be treated or purified through inlet pipe 17 and out concentrated waste product pipe 18, which is connected to three-way valve 19, controlled by combination valve controller, electronic logic means 16 to control the operation of the system and electric conductivity sensor 20 to monitor ionic concentration of the purified liquid, which also controls outlet valve 21. Bladder tank 22 serves to store the purified solution and maintain pressurization.

Fig. 6 shows a central flow design capacitor. 10 understood that any design which allows an equal fluid flow between cells, yet isolates individual cell compartments, may be used to make an enhanced voltage series, flow-through capacitor. For example, Fig. 6 shows a design with a central Capacitor stack 8 is placed inside cartridge flow path. 15 holder 23. Fluid flow is in through one of the inlets/outlets 24 and out the other one. Flow may be from the side, around the capacitor stack 8, through the holes 5, in gaskets 2, alongside electrode layers 1, and out central flow path 25. The central flow path 25 is formed by central holes in the 20 electrode, optional current collector 6 and spacer layer 4. The end single-sided electrode 1 is extended to form an anode or cathode lead 3 on each side. Screw 13 extends through cartridge holder 23 to form an electrical connection and leakproof seal with lead 3, by washer and screw means 14. Baffle 25 means 10 (not shown) may be inserted into the central flow path 25, in order to provide a long, thin cross-sectional flow path to isolate cells 7 with a high resistance electrical connection between cells 7 . For example, a spiral flow path baffle that forces fluid to spiral flow into the center of the 30 tube will provide such a flow path. Air bubbles or air gaps will also serve to isolate individual cells, yet allow fluid to flow and distribute evenly between cells.

require any spacer to prevent short-circuiting beyond the gasket material. After repeated uses, the old electrodes are replaced and sent to a smelter for recovery.

Example 5

5

The capacitor of Example 4 is manufactured with activated carbon cloth electrodes. Instead of replacing the electrodes, they are acid-washed in order to recover the metal in a concentrated acid solution. The cleaned electrodes may then be used in another purification cycle. Polarity is reversed every charge cycle, in order to help keep the electrodes clean.

Claims

What is claimed is:

5

10

15

20

30

35

Claim 1. A flow-through capacitor for the purification of an electrolyte fluid, which capacitor comprises:

- a) a cartridge holder;
- b) an inlet in the holder for a fluid to be purified;
- c) an outlet in the holder for the withdrawal of a purified fluid;
 - d) a discharge outlet; and
- e) a plurality of electrolyte-isolated individual cells, each cell composed of an anode-cathode pair of electrode material in a stacked arrangement within the holder, and the individual cells are electrically connected in series.
- Claim 2. The capacitor of claim 1 wherein the voltage of the stacked arrangement is higher than the individual cell voltage rating.
 - Claim 3. The capacitor of claim 1 wherein the stacked arrangement is characterized by a generally central, flow-through hole in the stacked electrode material.
 - Claim 4. The capacitor of claim 1 wherein the electrode material forms individual cells with a single facing anode on one side and a cathode on the other side of each cell.
- Claim 5. The capacitor of claim 1 which includes a gasket to form electrolyte fluid-tight individual cells, whereby the electrolyte of each individual cell is electrically isolated from neighboring cells.
 - Claim 6. The capacitor of claim 1 wherein the electrode material is selected from the group consisting of ruthenium oxide; activated carbon cloth; conductive metal foil; and metal conductive foil material coated with conductive particulate material.
 - Claim 7. The capacitor of claim 1 wherein at least one electrode comprises multiple parallel electrodes in an individual cell.

Claim 8. A capacitor system which comprises a plurality of the capacitors of claim 1, the capacitors electrically connected in parallel and with the fluid flow through the capacitor in series flow.

Claim 9. A capacitor system which comprises:

a) a first capacitor of claim 1;

5

- a second capacitor of claim 1, which is flowconnected in tandem with the first capacitor;
- c) a direct current-direct current (DC-DC)

 10 converter, transformer, or coil electrically connected to the first and second capacitors to recover energy from the discharge of the capacitor;
- d) a power supply for said capacitor, whereby in a cyclic operation, the first capacitor is charged and purifies a fluid from which the second capacitor is electrically discharged and absorbs a concentrated waste from the fluid, and the converter receives the electrical discharge from the second capacitor and increases the discharge voltage and charges the first capacitor.

20 Claim 10. A capacitor system which comprises:

- a) the capacitor of claim 1;
- b) a power supply for the capacitor;
- c) a source of fluid to be purified;
- d) a pump to introduce fluid to be purified into
 25 said capacitor;
 - e) a storage tank to receive purified fluid from the outlet for purified fluid and to maintain pressure in the system;
- f) a conductivity sensor to monitor ionic30 concentrations of the purified fluid;
 - g) a valve means to control the flow of the fluid in the system; and
 - h) a logic means to control the operation of the system responsive to the sensor.

Claim 11. A capacitor system wherein the capacitor of claim 1 comprises a module unit and which system comprises a plurality of module units electrically and fluid flow connected for purification of a fluid.

- Claim 12. A method for the purification of an electrolyte fluid having fluid waste contaminants, which method comprises:
- a) introducing the fluid into an inlet of a flowthrough capacitor;
- b) withdrawing a purified fluid from an outlet ofthe capacitor;

5

- c) discharging concentrated waste contaminants from a waste outlet of the capacitor;
- d) passing the fluid through a plurality of electrolyte-isolated individual cells, each cell composed of an anode-cathode pair of electrode material in a stacked arrangement within a holder, and the individual cells electrically connected in series.

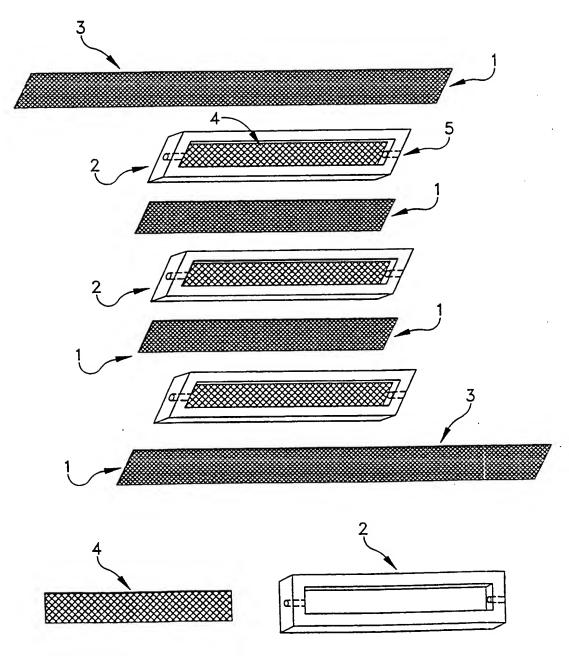


FIG. 1

PCT/US00/20768

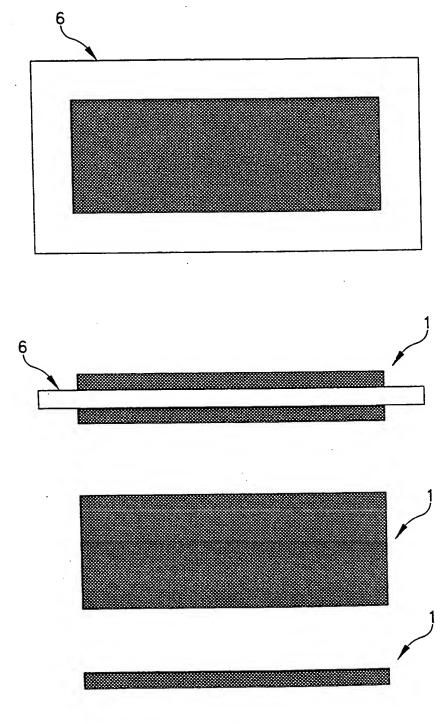
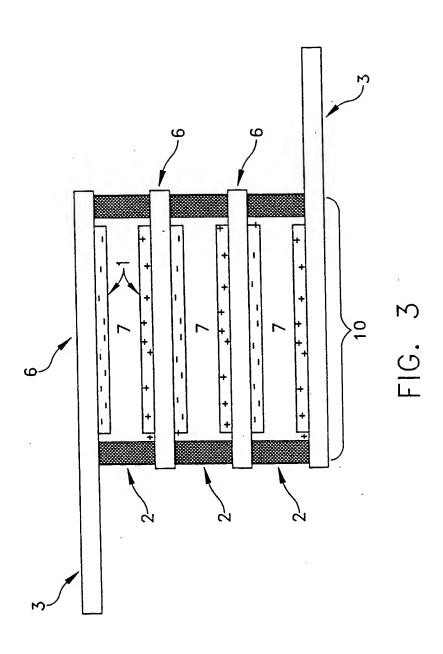
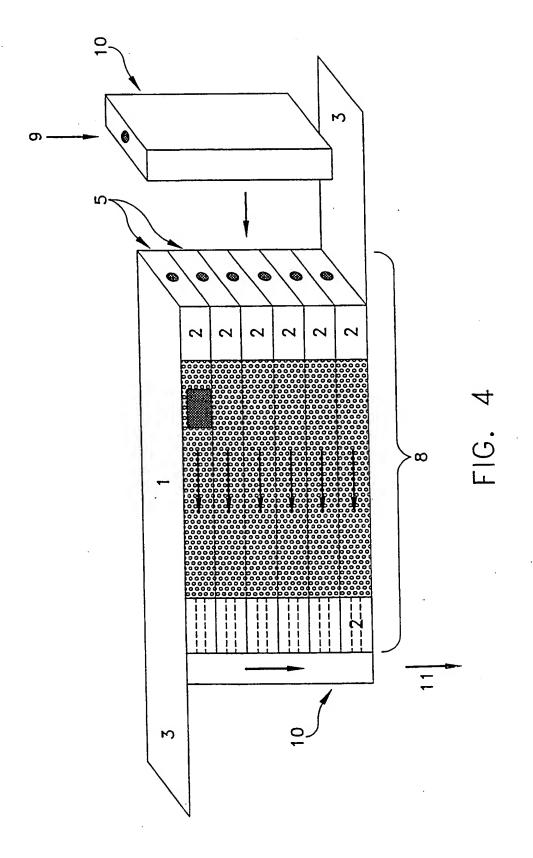


FIG. 2







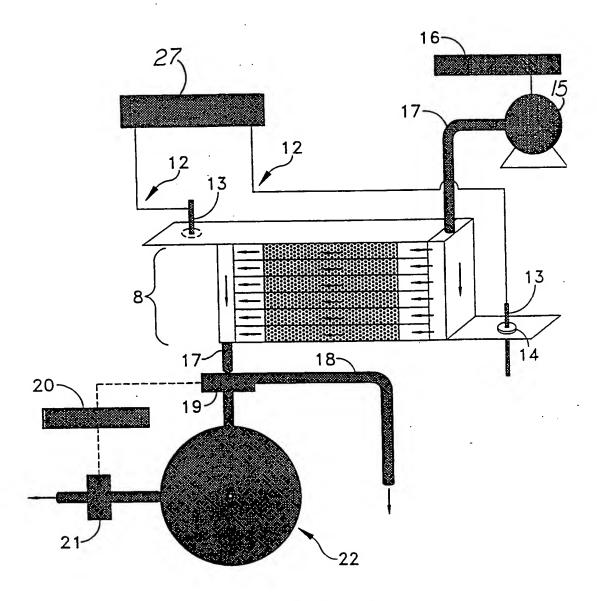
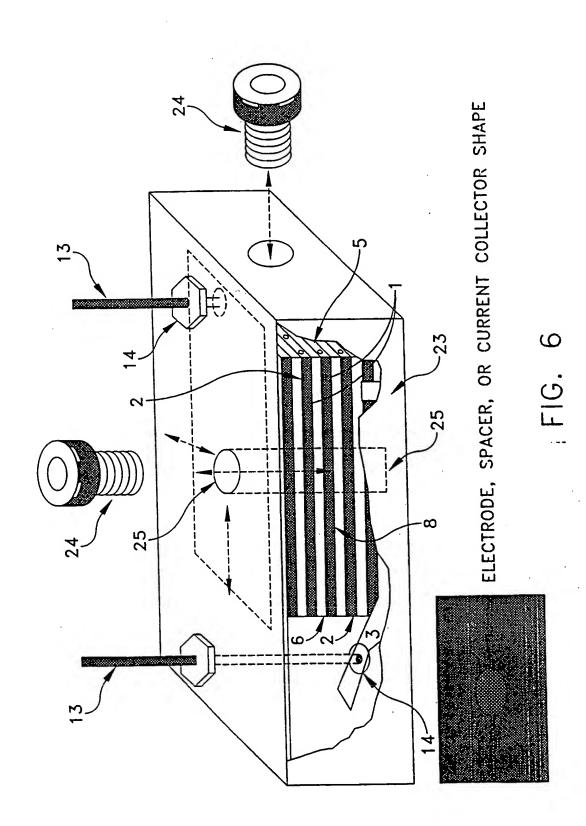


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No. PCT/US00/20768

A. CLASSIFICATION OF SUBJECT MATTER		
-IPC(7) :H01G 9/00, B01D 15/08 US CL :Please See Extra Sheet.		
According to International Patent Classification (IPC) or to b	ooth national classification and IPC	
B. FIELDS SEARCHED		
Minimum documentation searched (classification system follo	owed by classification symbols)	
U.S.: 361/502-503, 504, 508, 509, 517-519, 541, 536-	538; 210/198.2, 656	
Documentation searched other than mini: num documentation t	to the extent that such documents are included	in the field searched
NONE	to the extent and spon documents are morated	
Electronic data base consulted during the international search	h (name of data base and where practicable	search terms used)
USPTO APS WEST, EAST and title search	n (lame of data onse and, where proceeding	
C. DOCUMENTS CONSIDERED TO BE RELEVAN	NT .	
Category* Citation of document, with indication, whe	ere appropriate, of the relevant passages	Relevant to claim No.
Y US 5,793,603 A (LYMAN) 11 Aug document.	US 5,793,603 A (LYMAN) 11 August 1998 (11.08.1998), see entire document.	
Y US 5,748,437 A (ANDELMAN) entire document.	US 5,748,437 A (ANDELMAN) 05 May 1998 (05.05.1998), see entire document.	
US 5,779,891 A (ANDELMAN) 14 July 1998 (14.07.1998), see entire document.		12 10-11
Further documents are listed in the continuation of	Box C. See patent family annex.	
Special categories of cited documents:	"T" later document published after the in date and not in conflict with the appli	ternational filing date or priority
"A" document defining the general state of the art which is not const to be of particular relevance	idered principle or theory underlying the ir	vention
E earlier document published on or after the international filing	date X document of particular relevance; t considered novel or cannot be consid	he claimed invention cannot be lered to involve an inventive step
L document which may throw doubts on priority claim(s) or where the cited to establish the publication date of another citation or	hich is when the document is taken alone other Y* document of particular relevance:	he claimed invention cannot be
special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or	considered to involve an inventive	e step when the document is ch documents, such combination
P document published prior to the international filing date but late	•	
Date of the actual completion of the international search	Date of mailing of the international se	earch report
27 SEPTEMBER 2000	1 4 NOV	2000
Name and mailing address of the ISA/US	Authorized officer	
Commissioner of Patents and Trademarks		· (:
Washington, D.C. 20231	NGUYEN HA (Telephone No. (703) 308-6023	lens History

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No. PCT/US00/20768

A. CLASSIFICATION OF SUBJECT MATTER: US CL :		
361/502-503, 504, 508, 509, 517-519, 541, 536-538; 210/198.2, 656		
·		
	·	
	_	
·		
•		